ENABLING HIGH-ENERGY/HIGH-VOLTAGE LITHIUM-ION CELLS: PROJECT OVERVIEW

ES253

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2016 U.S. DOE HYDROGEN and FUEL CELLS PROGRAM and VEHICLE TECHNOLOGIES OFFICE ANNUAL MERIT REVIEW AND PEER EVALUATION MEETING

OVERVIEW

Timeline

- Start: October 1, 2014
- End: Sept. 30, 2017
- Percent complete: 50%

Budget

- Total project funding:
  - FY15 - $3000K
  - FY16 - $4000K
- ES252, ES253, and ES254

Barriers

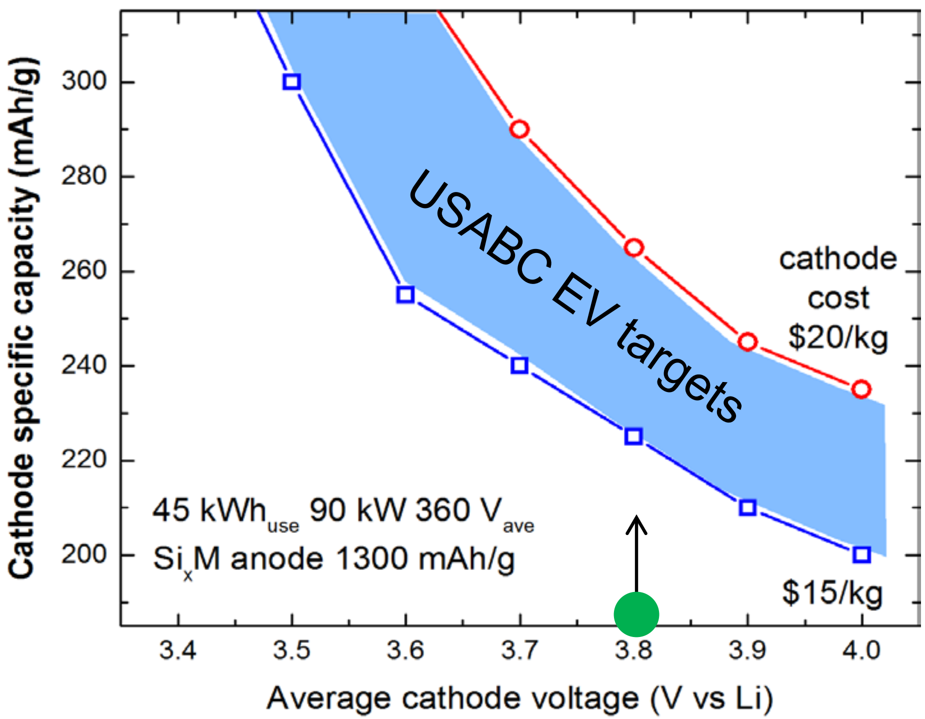
- Development of PHEV and EV batteries that meet or exceed DOE and USABC goals
  - Cost, Performance, and Safety

Partners

- Oak Ridge National Laboratory
- National Renewable Energy Laboratory
- Lawrence Berkeley National Laboratory
- Argonne National Laboratory

RELEVANCE

- Current cathodes: ~150-180 mAh/g at ~3.5-3.8 V (Li) giving <700 Wh/kg_{oxide} ( )
- Charging to higher voltages can increase energy: HV >4.3 V vs. graphite



<u>High voltage instabilities:</u>

- oxygen loss
- metal dissolution
- electrolyte oxidation
- TM migration/bulk limits
- SEI/CEI/impedance
- …

↕

<u>Key Objective</u>:
fundamental understanding

HV instabilities must be overcome to take full advantage of NMC-based cathodes

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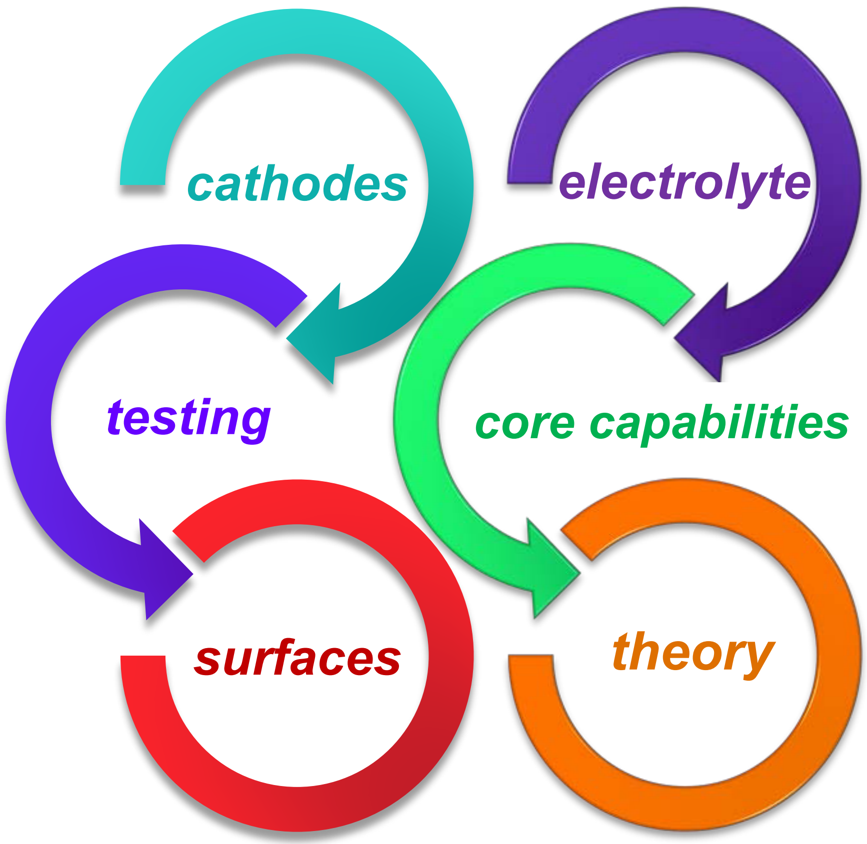
APPROACH: PROJECT THRUSTS



Flexibility

- Designations not stringent
- Focus on identifying problems
- Establish collaborations as needed

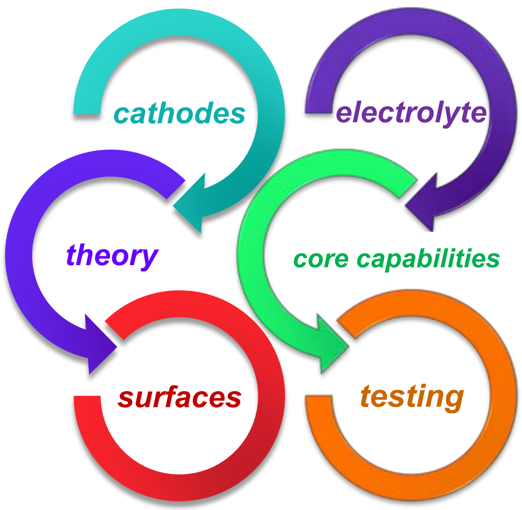
- ***understanding of HV processes***
- ***new materials***
- ***validation of full-cell, pouch-cells***

Subgroups within the overall project have been formed to define and focus on specific, correlated challenges of high voltage operation

Oak Ridge National Laboratory NREL National Renewable Energy Laboratory Berkeley Lab Argonne National Laboratory

APPROACH: PROJECT MANAGEMENT

Organization



- Designated team leads and members with relevant expertise
- Working within and across teams to address challenges

Communication

- Weekly, full-team meetings with research updates, discussions, and project info
- Periodic, full-team "reviews" to inform project focus
- Online database of all project data/protocols/info accessible to all team members

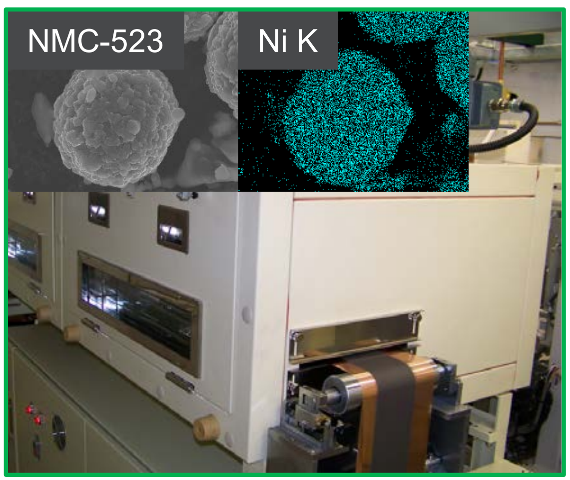
Focus

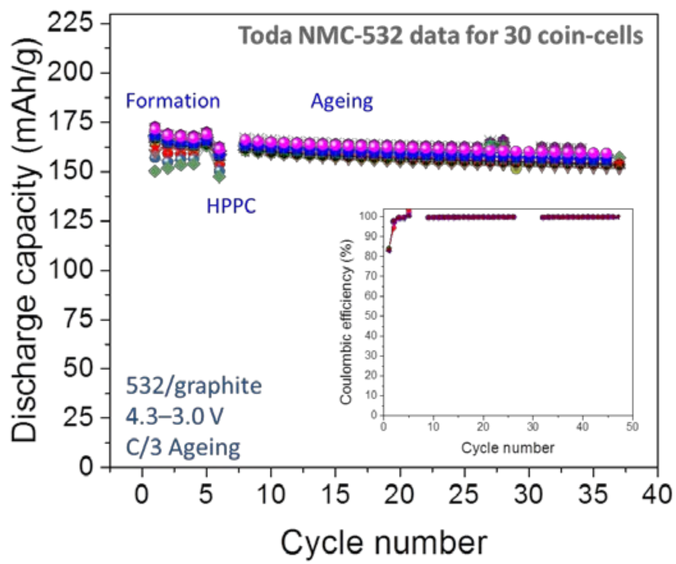
Communication protocols used to assess progress and define future direction

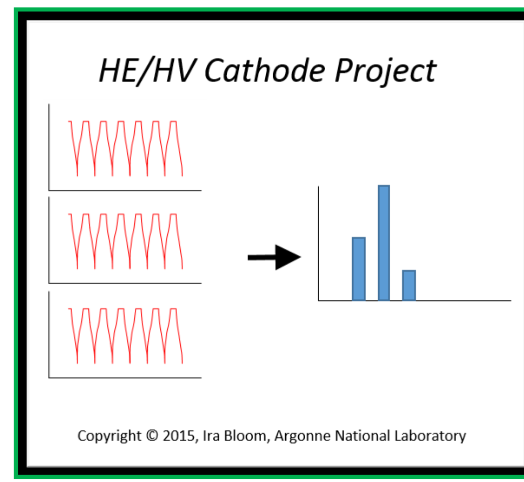
- Based on FY15/16 work the HV team has begun to focus major efforts on ***surfaces***
- Priority tasks have been identified and *"Sprint"* teams formed to address challenges

APPROACH: STANDARD PROCEDURES

- ***Standard***, high-quality *materials* distributed and utilized project-wide
- ***Standard*** *testing protocols* distributed and utilized project-wide
- ***Standard*** *analysis* enabled via custom software distributed project-wide







Standardized materials/protocols are critical to the success of multi-lab efforts

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PROGRESS: *MATERIALS* – BASELINE AND SPECIALTY

Electrode Library ID	Material	TTL Loading (mg/cm^2)	Full Cell Voltage Window
A-A002A	Phillips A12 Graphite	5.88	
A-A004A	NEI LTO	13.32	
A-A005A	Superior Graphite SLC1520P	6.28	
A-C011	ECOPRO NCM 622	10.03	4.2V
A-C013A	Toda NCM 523	11.33	4.2V
S-C002	Toda NCA	11.59	4.2V
A-C015	Toda NCM 523	9.17	4.4V
A-C016	Toda NCA	8.79	4.4V
A-C017	Toda HE5050 (LMR-NMC)	6.06	4.4V
A-C018	ECOPRO NCM 622	8.82	4.4V

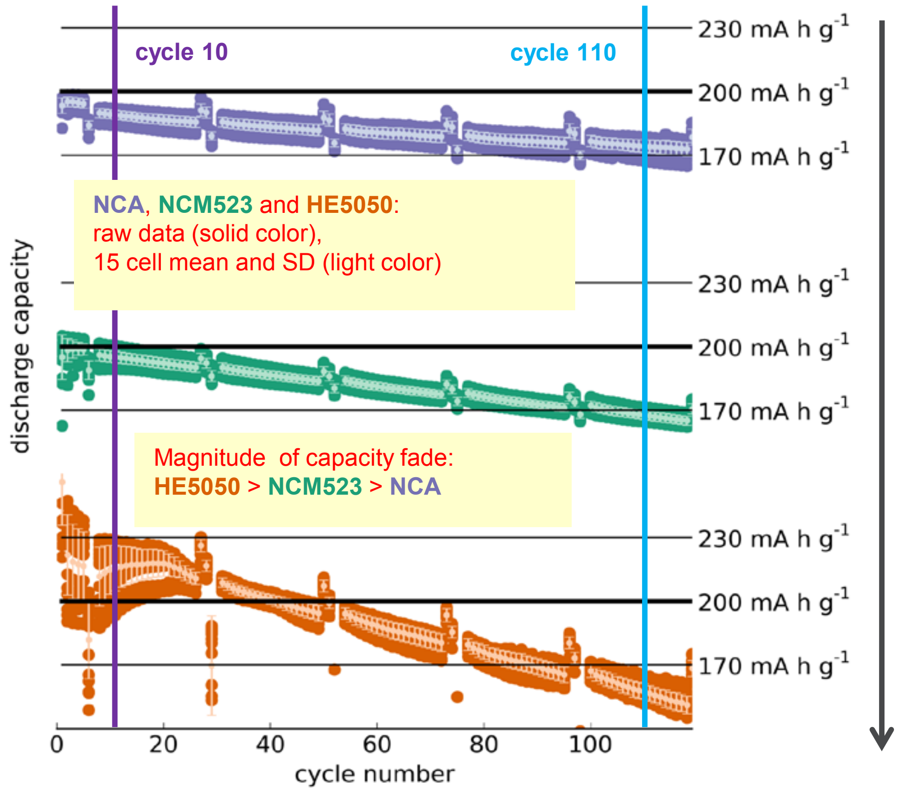
Special Request Electrodes	Loading (mg/cm^2)
Toda 523+C45+5130	4.08
NCM 622 + C45 + 5130	10.21
NEI LTO + C-45 + 9300	24.83
NEI LTO + C-45 + 9300	24.83
Toda 523(2nm ALD Al2O3) + C45+5130	11.37
Toda 523(2wt% Al2O3 WC) + C45+5130	11.28
Toda 523(1nm ALD Al2O3) + C45+5130	11.25
NEI LTO + C-45 + 9300	19.75
NEI LTO + C-45 + 9300	24.83
NEI LTO + C-45 + 9300	19.65
MERF LL, ES-20150514 + C45 + PVDF	8.96
MERF LL, ES-20150514 + C45 + PVDF	8.96
Toda 523(2C ALD Al2O3) + C45+5130	9.22
Toda 523(2C ALD Al2O3) + C45+5130	11.09
Toda 523(4C ALD Al2O3) + C45+5130	9.22
Toda 523(4C ALD Al2O3) + C45+5130	11.38
Toda 523+ C45 + 5130	4.08
Toda 523+ C45 + 5130	4.08
Toda 523+ C45 + 5130	4.46
Toda 523+ C45 + 5130	4.08
A12 Graphite+ SP+9300+ Oxalic Acid	6.06

A total of ***429*** *Electrode Sheets* (**10.4** sq. meter) of Specialty Electrodes have been distributed. (to date)
Additionally, a total of **6300** grams of cathode powders have been distributed to researchers in this project. (ANL, ORNL, NREL, LBNL)

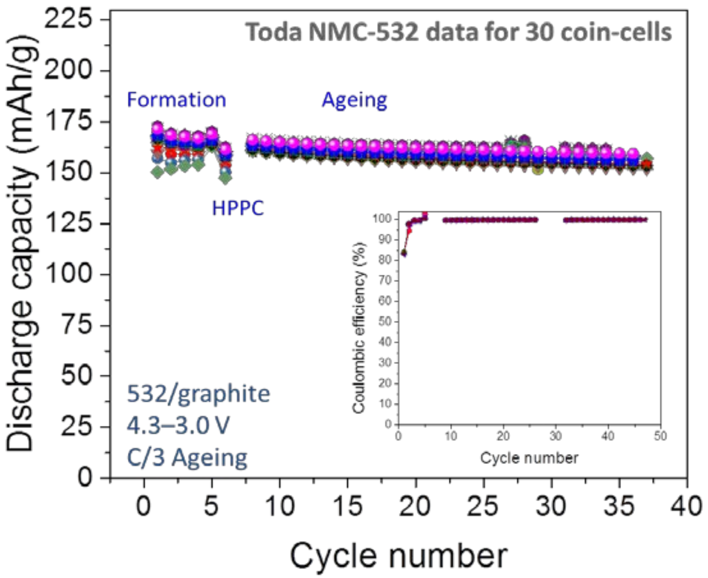
CAMP facility – standardized materials, electrode fabrication, and distribution

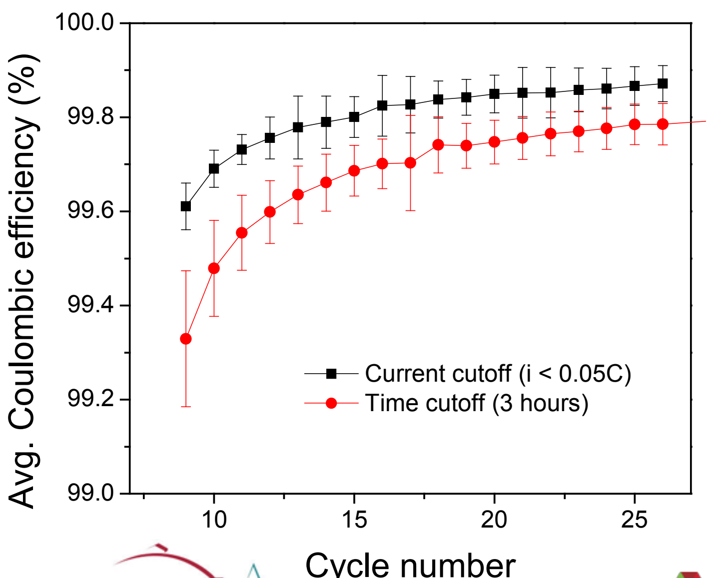
PROGRESS: *PROTOCOLS* – CYCLING

Baseline data for three cathode materials



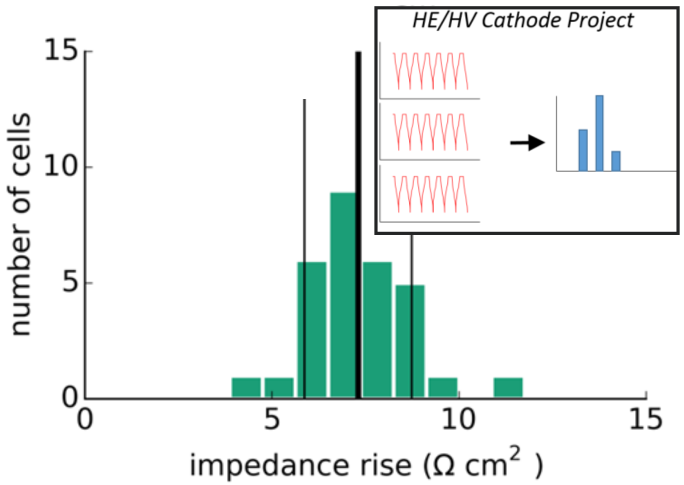
Statistical evaluation of coin-cell data

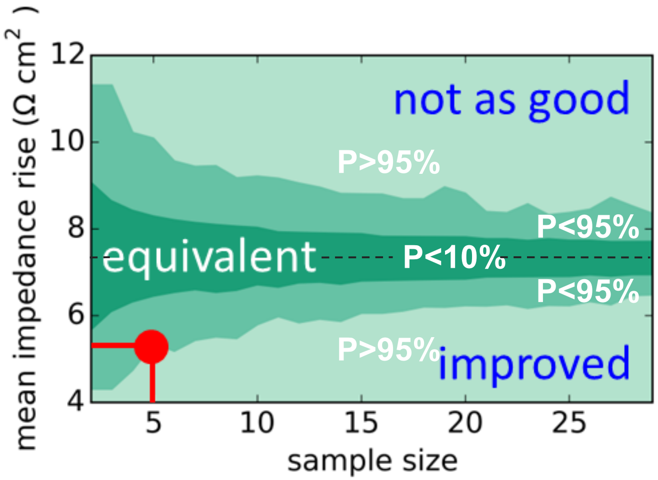




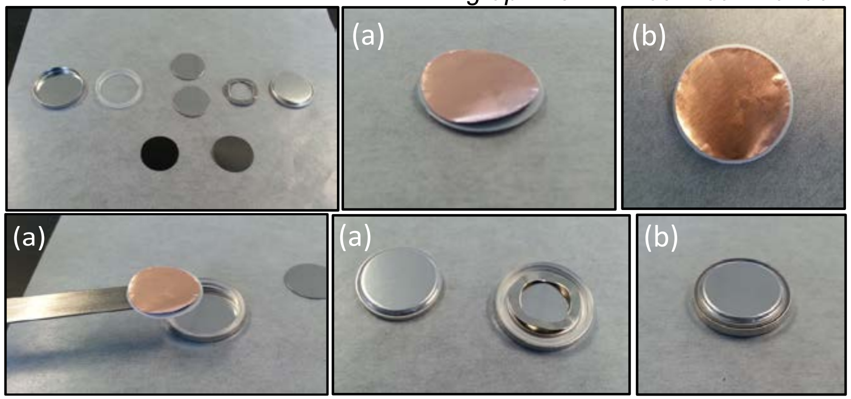
All baseline and developed systems are tested, analyzed, and compared under the same cycling protocols

PROGRESS: *ANALYSIS* (see ES252)





graph from HV coin-cell manual



Procedures for all aspects of coin-cell testing have been written and distributed

- Coin-cell data must be statistically verified
- Skill-of-the-worker is a significant factor
- Project has a dedicated team for verification of promising materials/results

Data analysis derived from baseline statistics for confident identification of trends

PROGRESS: *ANALYSIS* – COIN/POUCH CELL CORRELATION

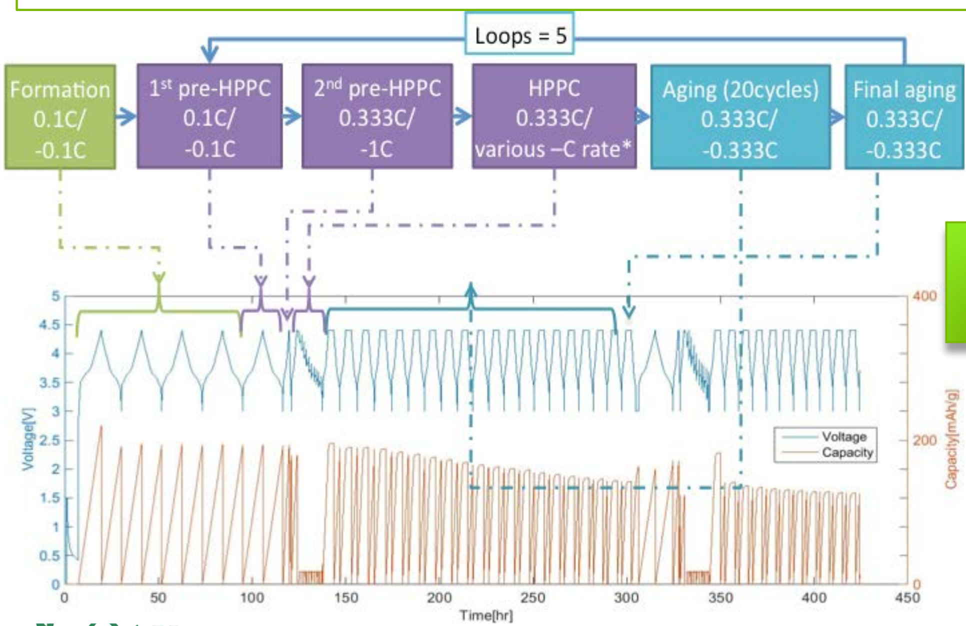
Electrolyte volume factor group, *F*	Electrolyte volume to pore volume ratio, *f* 5 cell ave for each group
F 1.3	1.25, 1.29, 1.29, 1.33, 1.32 (from cell #1 to #5)
F 1.9	1.89, 1.94, 1.89, 1.93, 1.90 (from cell #6 to #10)
F 2.5	2.54, 2.50, 2.42, 2.42, 2.62 (from cell #11 to #15)
F 3.0	2.85, 3.10, 3.14, 3.16, 2.94 (from cell #16 to #20)
F 3.5	3.51, 3.52, 3.55, 3.49, 3.56 (from cell #21 to #25)

- Test samples: 70 mAh LIBs
- Electrodes: A12 graphite
  $LiNi_{0.5}Mn_{0.3}Co_{0.2}O_2$
- Electrolyte: 1.2 M $LiPF_6$ in EC:EMC

$$F = \frac{\textbf{Electrolyte volume}}{\textbf{Pore volume}}$$

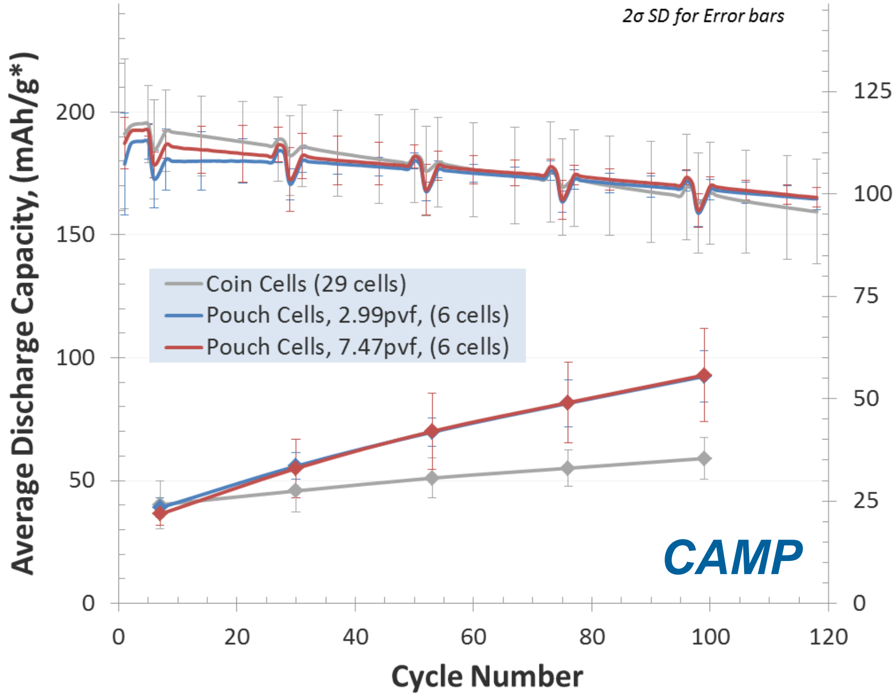
in electrodes and separator

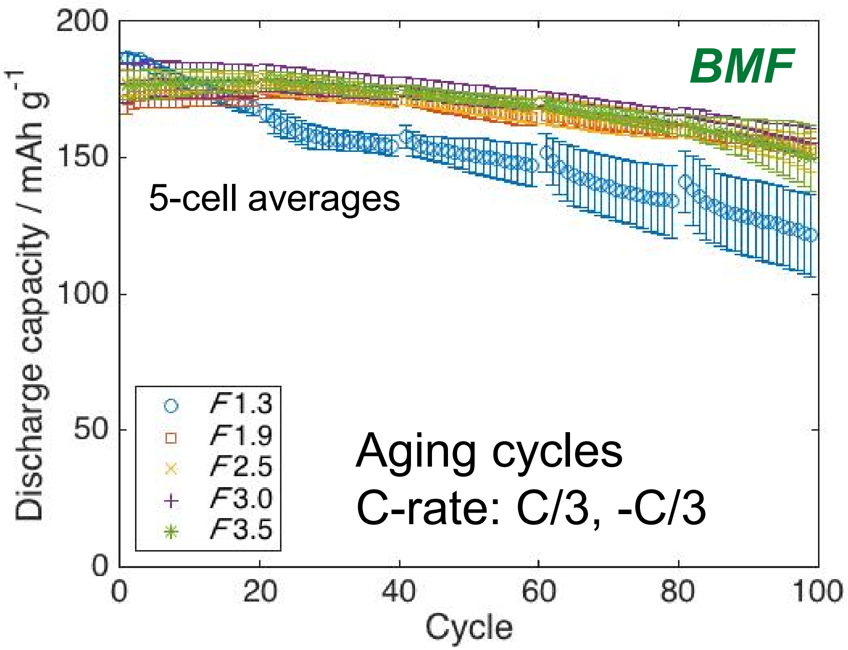
Test protocol with cut-off voltages at 3 V and 4.4 V



1. Capacity fade during 100 aging cycles
2. C-rate tests at every 20 aging cycles
3. Resistance analysis from HPPC
4. Impedance spectroscopy analysis for Ohmic resistance and resistance from passivation layer and charge transfer.
5. XPS analysis for transition metal dissolution study
6. Differential voltage analysis for irreversible lithium transfer from NMC to A12 graphite

PROGRESS: *ANALYSIS* – COIN/POUCH CELL CORRELATION





- Previous coin-cell studies showed that electrolyte volumes of ~3x the total pore volume (electrodes and separator) were optimum
- Detailed studies of 40 mAh and 70 mAh, single-layer pouch cells showed good correlation with coin-cell data (slightly higher imp. for PCs) → ***multi-layer cells?***

Coin-cell trends can be used to inform decisions on scale-up and larger format testing

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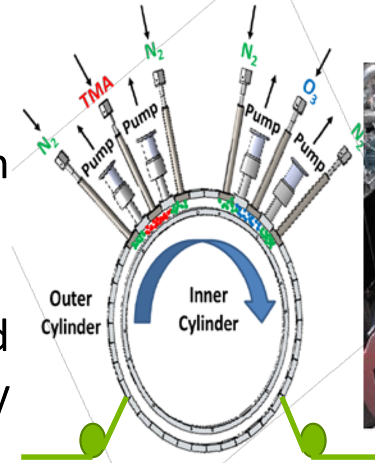
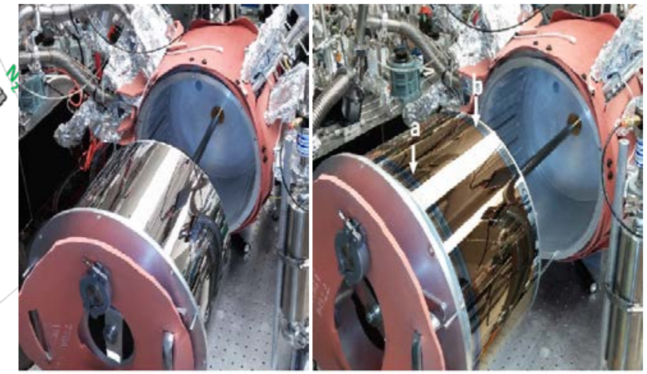
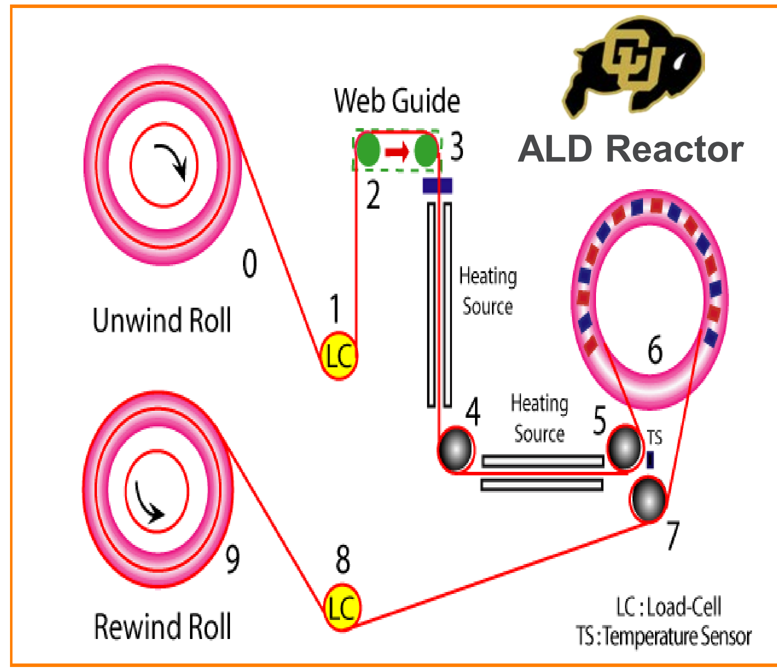
PROGRESS: *MATERIALS* – ELECTRODE COATINGS

ROLL-TO-ROLL (R2R) ALD

- Able to coat 3’ by 8” laminates in rotary reactor mode
- Currently being integrated with unwind -rewind system under complementary NSF effort
- Initial coating process development focused on alumina on baseline NMC materials (oxides, sulfides, nitrides)



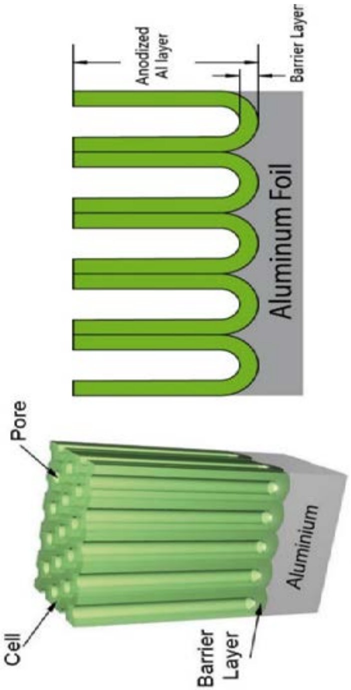




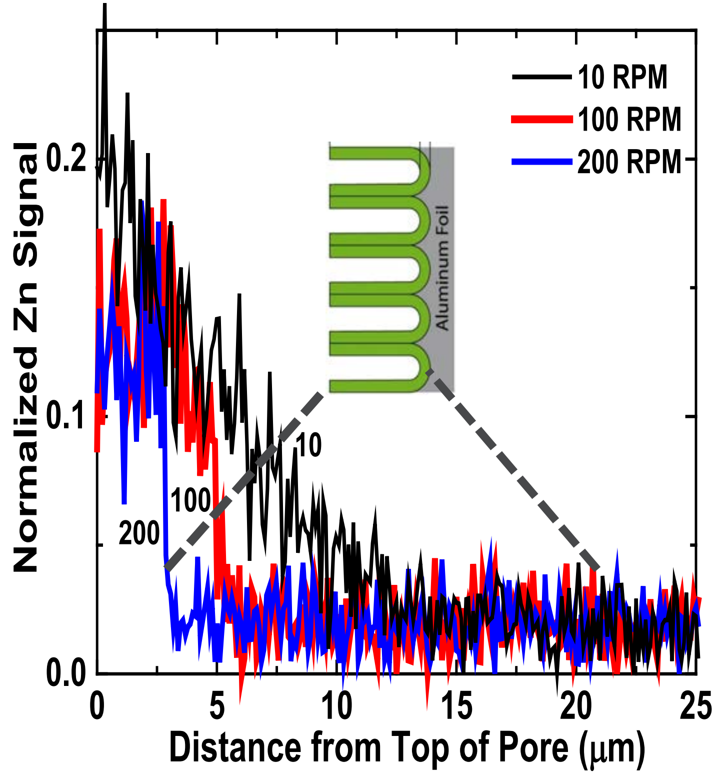
Project Objective

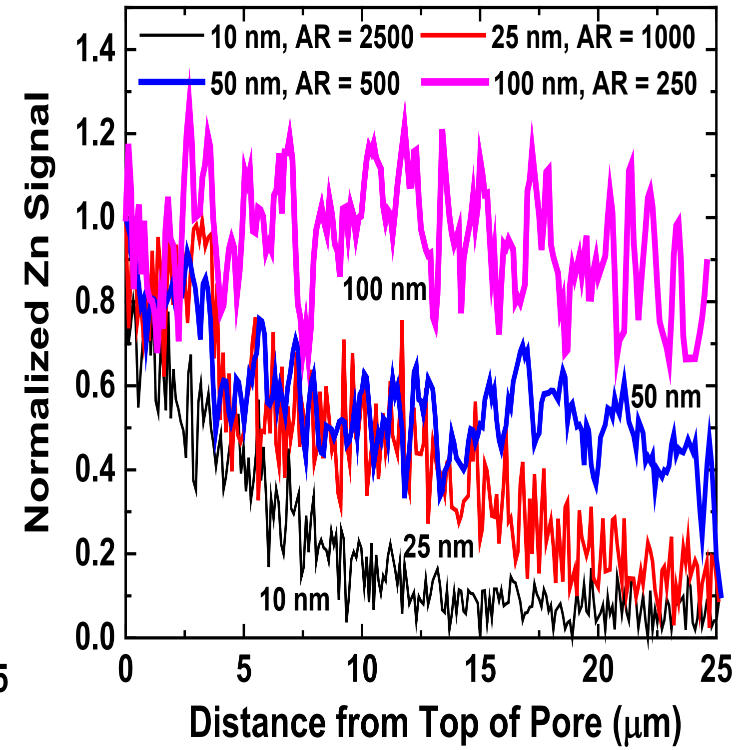
Develop standardized and well-defined thin films for detailed mechanistic studies on surface protection of baseline NMCs (static and R2R, powders/laminates)

PROGRESS: *MATERIALS* – R2R COATINGS



model substrates

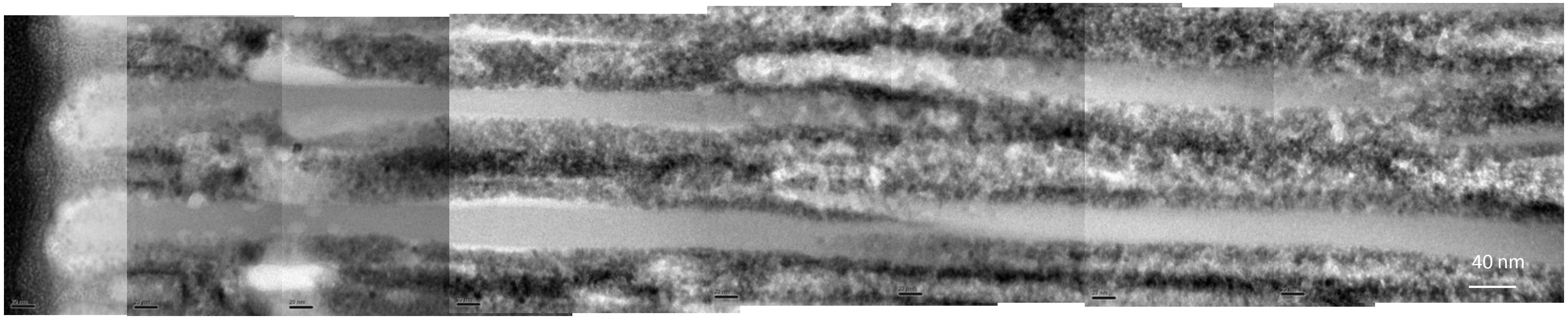




Pore Diameter = 10 nm	Pore Diameter = 25nm	Pore Diameter = 50 nm	Pore Diameter = 100 nm
10 RPM	10 RPM	10 RPM	10 RPM
100 RPM	100 RPM	100 RPM	100 RPM
200 RPM	200 RPM	200 RPM	200 RPM

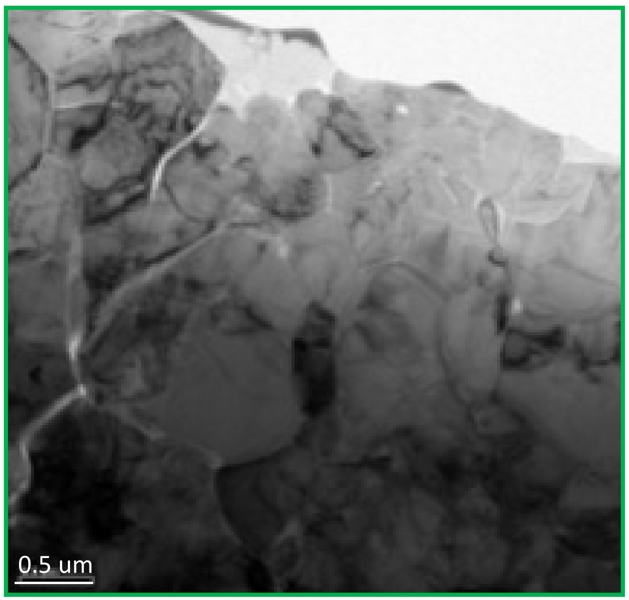
Coating conditions must be optimized for porosity of substrates (electrodes)

PROGRESS: *MATERIALS* – R2R COATINGS



1 um

NCM 523 laminate from CAMP

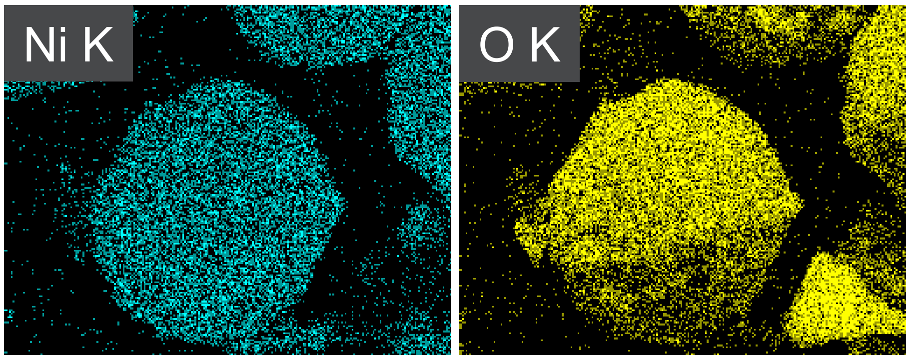


- TEM results appear to indicate that precursor penetration into laminate may be limited.
- Precursor residence time and electrode calendaring are important parameters
- Studies on cathode powders are also ongoing

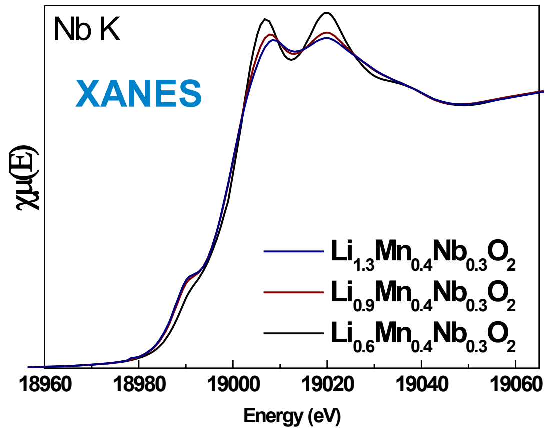
Processing of well-defined, uniform films for R2R electrode coatings is not trivial

PROGRESS: *MATERIALS RESEARCH* (see ES254)

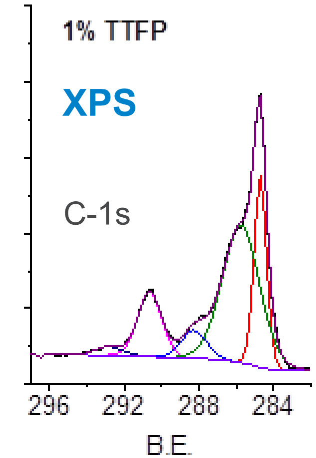
alternative coating strategies



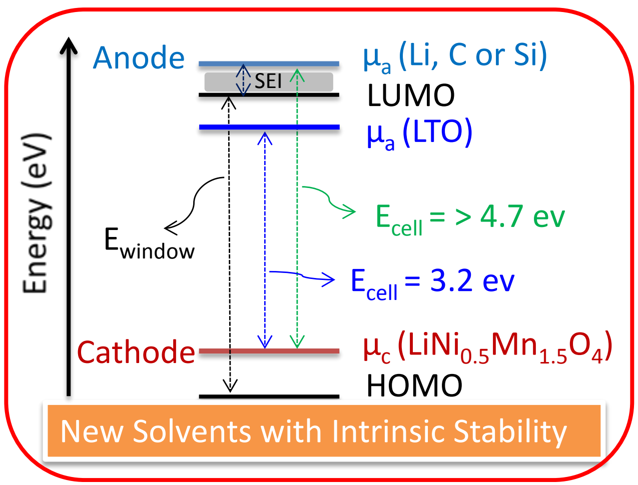
study of model systems



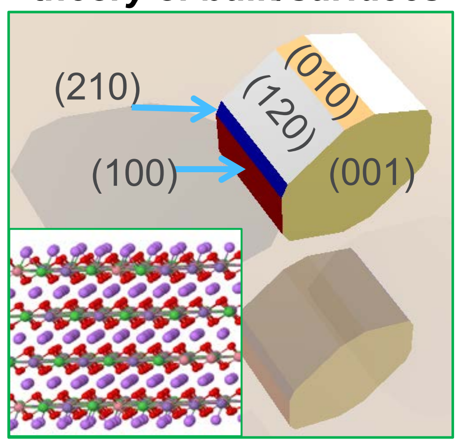
additives/surfaces



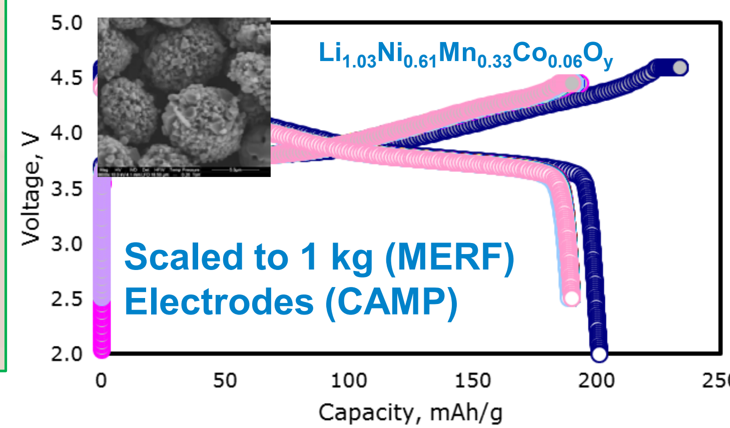
Design/synthesis of HV electrolytes



theory of bulk/surfaces



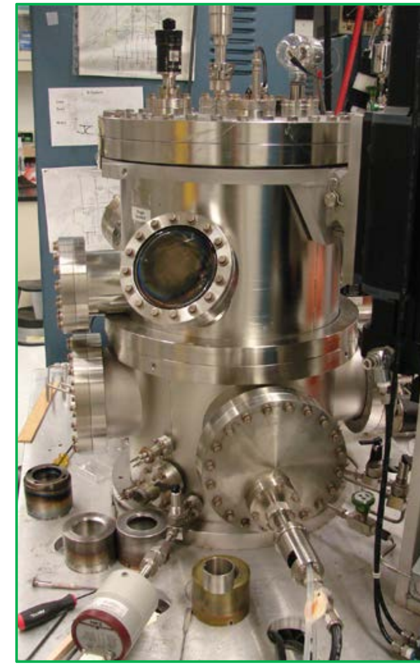
Design/scale-up of new cathodes



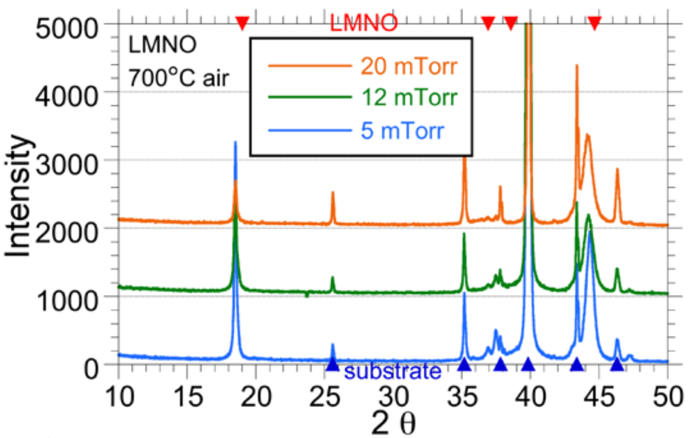
Large effort on understanding/design/synthesis/testing of ***new*** materials

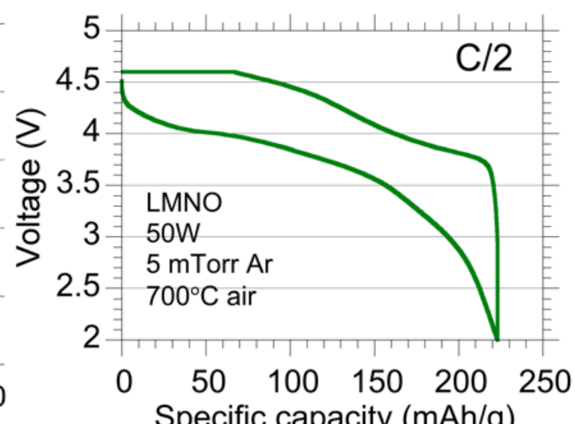
PROGRESS/FUTURE WORK: THIN FILM CATHODES

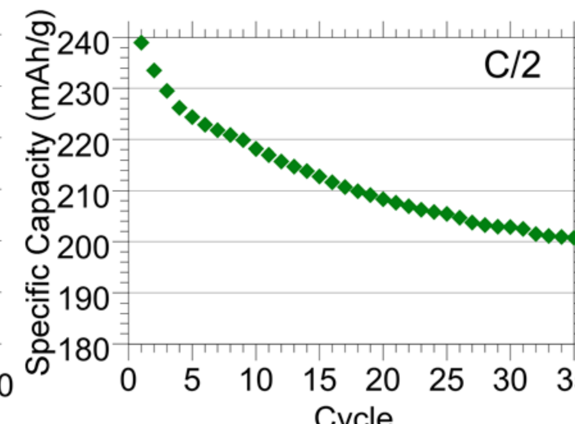
Thin films provide planar, single-phase cathodes that are well-suited for in-depth, ***interfacial*** characterization



- Progress to date
  - Identified processing conditions to give thin films of desired phase and composition
  - Initial cycling shows expected voltage profile, capacity, and stability
- Future
  - Examine interface for changes due to cycling
  - Produce thin films of NMC-532, NMC-622, and NCA

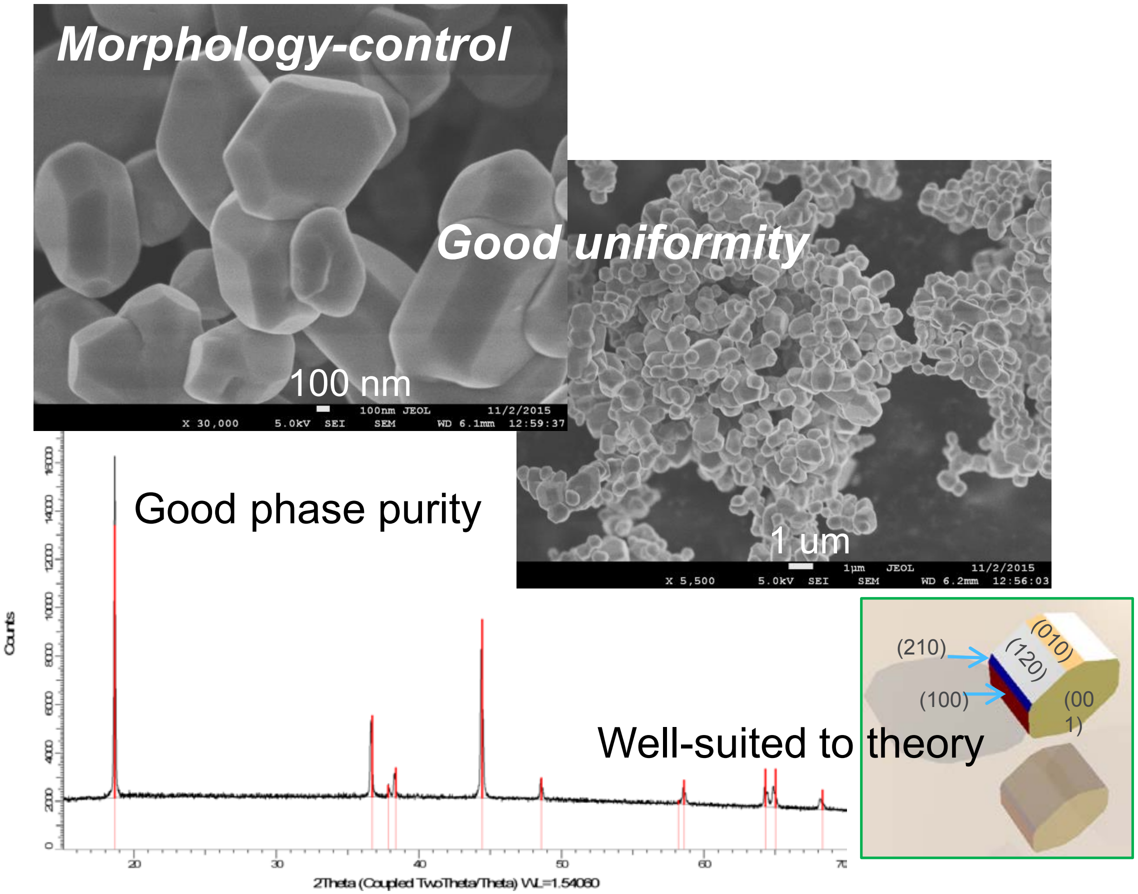




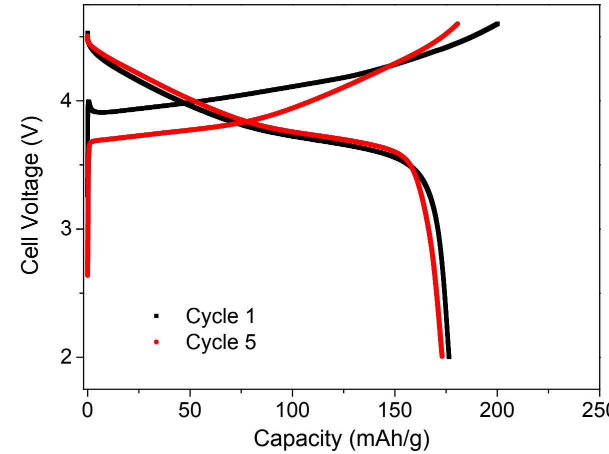


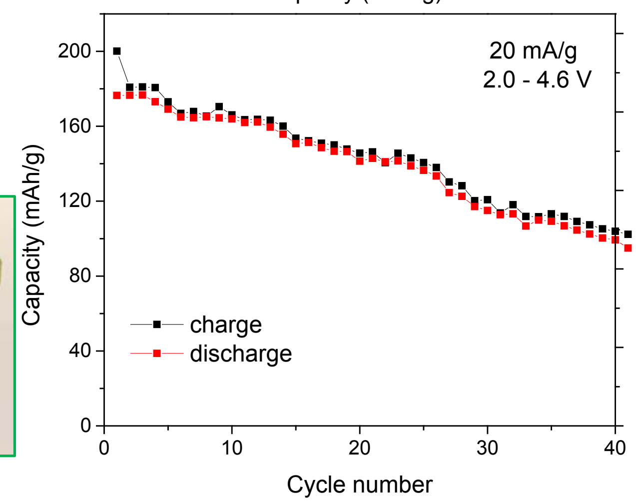
PROGRESS/FUTURE WORK: SINGLE-CRYSTAL NMCS

- Micron-sized NMC532 crystals prepared from Ni, Mn and Co nitrates in a CsCl flux, 850°C for 8 h.



Good Performance





Well-defined morphologies of NMCs for unique *surface* studies/characterization

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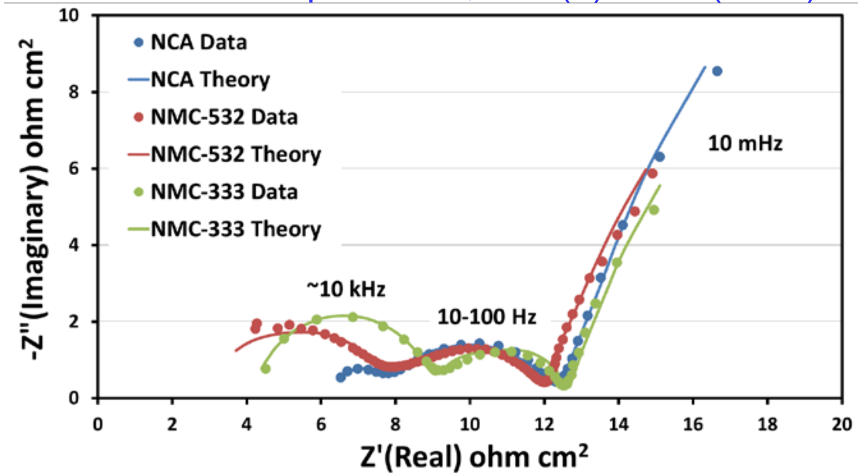
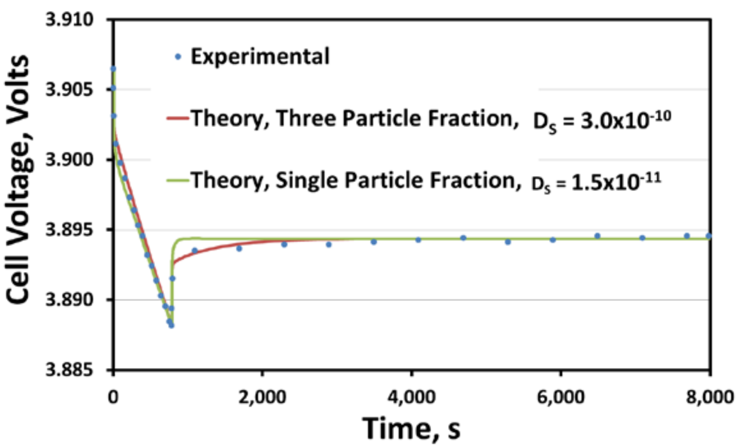
PROGRESS/FUTURE WORK: BULK/INTERFACE MODELING

model description *JES*, **162** (4) A559 (2015)



- EIS model analysis of micro-reference electrode cell studies are able to track changes in interfacial transport and kinetic parameters with SEI and surface modifications.
- Not apparent from EIS and short current pulse studies, the lithium transport in NMC-532 active material shown to be more complex compared to NCA and NMC-333.
- As an example, Galvanostatic Intermittent Titration Technique (GITT) studies on NMC-532 gives rise to an extremely long relaxation time constant that can be modeled using multiple active material particle fractions.

NMC-532 Half-Cell GITT ($X_S = 0.52$)
13m C/21 Discharge Followed by Long Rest



(see ES254)

Models are being developed to understand complex bulk/interfacial processes

FUTURE WORK

- Explore correlations between larger-format, multi-layer pouch cell data and baseline, coin-cell data (e.g., pressure effects, gas analysis, graphite options)
- Finalize conditions for optimized, static ALD ***surface*** coatings and begin protocol testing in full-cells. Initiate electrochemical studies on R2R electrode coatings
- Initiate detailed studies of ***surface reactions*** on ***surface-modified***, thin film, NMC cathodes
- Detailed studies of ***surface termination, migration, & reactions*** on single-crystal NMC particles
- Mechanistic studies of ***surface interactions*** of fluorinated electrolytes with NMC surfaces (Identified as a priority task – subgroup has been formed)
- Mechanistic studies of ***surface interactions*** of select electrolyte additives with NMC surfaces (Identified as a priority task – subgroup has been formed)

Major effort going forward will focus on understanding surface/interfacial processes

SUMMARY

- High-voltage NMCs are important for advancing lithium-ion for transportation applications – challenges need to be addressed on a fundamental level
- Large effort in establishing best conditions for success of this multi-lab project – materials, baselines, protocols, and organization
- FY15/16 work has been evaluated and project direction refined to give emphasis to issues of surface degradation
- Priority tasks have been established and dedicated teams assigned to shorter-term projects to accelerate advances in important areas
- Significant progress has been made in materials research/characterization
- Collaborative efforts on unique surface-related studies have been established involving the correlated capabilities of all four labs and are currently ongoing

CONTRIBUTORS AND ACKNOWLEDGMENT

Research Facilities

- Post-Test Facility (PTF)
- Materials Engineering Research Facility (MERF)
- Cell Analysis, Modeling, and Prototyping (CAMP)
- Battery Manufacturing Facility (BMF)
- Advanced Photon Source (APS)

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